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A One-Step, Organic-Solvent Processable Synthesis of PEDOT Thin Films via *in Situ* Metastable Chemical Polymerization

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ABSTRACT: A straightforward approach to the synthesis of electrically conducting PEDOT thin films using metastable and organic-solvent processable mixtures that rapidly polymerize upon solvent evaporation is presented. This one-step synthetic procedure, previously used to prepare well behaved polypyrrole and polythiophene films, has now been extended to one of the most academically/industrially studied and commercially successful polythiophene-based polymers, PEDOT. The methodology can be used to synthesize smooth, uniform, homogeneous, crack and pinhole free, conducting (0.02−0.47 S/cm), and highly transmissive PEDOT films with well-defined spectroelectrochemistry by spin-coating organic-solvent processable mixtures of EDOT monomer and phosphomolybdic acid oxidant onto conductive and nonconductive glass substrates.

Introduction

In 1976 Heeger, Shirakawa, and MacDiarmid showed that π-conjugated organic-polymers could be made to conduct electrical charge over a wide range of values by simple oxidative doping.[1] This pioneering work stimulated multiple lines of inquiry directed toward exploiting this property for practical applications. In particular, Heeger envisioned that this new field of research, created at the boundary of chemistry and condensed matter physics, would produce a new generation of polymers that would combine the superior optical and electrical properties of metals with the excellent mechanical and processing advantages of polymers.[2] However, achieving this vision would not be straightforward. Conductivity and processability are mutually exclusive, or at minimum difficult to obtain in a single material, often requiring a judicious compromise between the two properties. For example, good conductivity is often associated with highly planar and strongly interacting π-conjugated polymers, whereas good processability is typically associated with highly twisted and weakly interacting π-conjugated polymers, making it difficult to simultaneously achieve sufficiently high conductivity and processability within one material.

One class of conducting polymer that has seen significant attention from both academia and industry, largely because of its diverse and often remarkable properties, is polythiophene-based polymers.[3] Unfortunately, relatively few viable technologies have emerged from proof-of-concept stage to full commercial realization because of processability problems. While ameliorating the processability of polythiophenes by adding bulky side chains is a common technique, it invariably leads to reduced conductivity due to diminished intramolecular $\pi-\pi$ interactions.[3] An alternative strategy, first described by Bayer AG research laboratories in the late 1980s involving emulsion polymerization of 3, 4-ethylenedioxythiophene (EDOT) and polystyrenesulfonate (PSS) in aqueous solution, was quite successful, resulting in the most commercially successful conducting polymer to date, namely poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT−PSS).[4,5]

The utility of PEDOT−PSS, a water-soluble dispersion that is readily cast into conductive, transparent, stable films, has been demonstrated in diverse applications including polymer light-emitting diodes (PLEDs),[6] photovoltaics,[7] antistatic coatings,[8] electrochromic displays,[9] supercapacitors,[10] solid state ion sensors,[11] biosensors,[12] and fuel cells.[13] PEDOT−PSS's greatest commercial and near commercial realization lies within technologies requiring PEDOT−PSS to perform relatively simple or monolithic tasks, such as electrical conduction in antistatic coatings for photographic film, and hole injection from hole injecting anodes in PLEDs. To fully exploit the remarkable properties of PEDOT that have made it the quintessential polythiophene polymer in current technological applications, and to incorporate these properties into novel technologies of the future will require straightforward methods of preparing thin films from organic-solvent processable forms of PEDOT.

For example, the development of conducting-polymer sensor array analogues of the mammalian olfactory system for odorant sensing applications (i.e., "electronic noses") requires deliberate control over the chemical properties of individual sensing elements in the array. This level of control has been achieved through the use of organic-solvent processable mixtures containing polypyrrole and insulating polymer, in which the organic-solvent processable polymers were added to tune the chemical sensitivity and selectivity of the sensors.[14] Because the organic-solvent processable sensor elements are chemically compatible with, or "recognize" (i.e., solubilize) organic-soluble odor molecules, an organic-solvent processable form of PEDOT that is capable of generating conducting, homogeneous composites of conducting and insulating polymer would be useful for this type of application.

In addition to "electronic nose" applications, organic-solvent processable forms of PEDOT are needed for PLED display applications because the exclusion or removal of moisture during device processing steps could improve device metrics and lower manufacturing costs. Recently, Kim et al showed that an organic-solvent processable form of PEDOT consisting of a dimethylformamide (DMF) dispersion of PEDOT and polyionic liquids (PILs) had improved device performance.[15] The lifetime improvement was partly attributed to the organic-solvent

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processable/hydrophobic characteristics of PEDOT−PIL. While PEDOT−PIL is a promising organic-solvent processable form of PEDOT, its multistep synthesis and requirement for a low vapor pressure/high boiling point organic solvent is far from ideal.

In addition to organic-solvent processable forms of PEDOT, researchers are exploring new methods/processes for preparing homogeneous, conductive, thin films, that can be grown simply and directly onto a substrate, thereby mitigating the compromises often seen between processability and performance when using PEDOT−PSS dispersions. There are currently three *in situ* polymerization methods being explored, including electropolymerization, *in situ* chemical polymerization, and vapor phase polymerization (VPP). While electro-polymerization[16] is relatively straightforward, requiring one to simply place two electrodes into a solution containing monomer and electrolyte, and cycling the potential to polymerize the monomer onto the electrode surface, it nontheless requires conducting substrates. In addition, film uniformity can often be a problem over large electrode areas because of inhomogeneous electric fields. Alternatively, *in situ* chemical polymerization, in which a mixture containing monomer, oxidant, and inhibitor is spun directly onto a substrate, followed by thermal initiated polymerization, has been used to deposit PEDOT films.[17] While this method allows for deposition onto both conducting and nonconducting substrates, its limitations are that immense skill is often needed to obtain homogeneous films and additional thermal processing steps are required that ultimately add cost and complexity to the overall process.[18] A third technique, that is quite popular, is VPP. While this method can give homogeneous thin films with high conductivity, it nontheless requires multiple processing steps including oxidant deposition, solvent removal, and careful control over water and monomer deposition rates in a humidity and temperature controlled atmosphere.[19−23] To circumvent some of the limitations of current *in situ* methods of PEDOT film formation, we have developed a straightforward, one-step approach to the synthesis of smooth, homogeneous, uniform, crack and pinhole free, highly transmissive, conducting films of PEDOT, grown directly onto nonconducting and conducting substrates using organic-solvent processable mixtures of monomer and oxidant. This one-step synthetic procedure was previously used to prepare well behaved polypyrrole[24] and polythiophene films[25] and is now extended to the synthesis of PEDOT thin films.

Experimental Section

Material and Chemicals. Phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}$) (PMA), 3,4-ethylenedioxythiophene (EDOT), and tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$) were purchased from Aldrich and used without further purification. HPLC grade acetonitrile, methanol, isopropanol (IPA), dichloromethane (DCM), and tetrahydrofuran (THF) were purchased from Fischer Scientific and used without further purification. Indium tin oxide (ITO, 6 ± 2 Ω/square) glass slides were purchased from Delta Technologies Limited and washed/sonicated for 10 min in each of an aqueous Fisherbrand Sparkleen detergent solution, deionized water, methanol, and isopropanol before drying under a stream of N_2. Fluorine doped tin oxide (FTO) coated glass slides were cut from Pilkington's Energy Advantage Low-E glass and subjected to the identical cleaning protocol used for ITO. Precleaned Fisher brand microscope glass slides were purchased from Fischer Scientific and used without further cleaning.

Synthesis. Two separate solutions, one containing EDOT monomer and the other containing PMA oxidant were mixed prior to spin-coating (i.e., all PEDOT−PMA films were prepared by initiating spin-coating within ca. 5 min of mixing). The resulting gold/green polymerization mixtures contained 0.2 M EDOT and 0.05−0.5 M PMA in acetonitrile or THF. Films were prepared by spin-coating mixtures onto either plain glass substrates (nonconducting) or FTO/ITO coated glass substrates at 2000 rpm for 10 s. The brown/black films were allowed to dry at room temperature for 30 min before rinsing with an ∼3% v/v IPA/DCM mixture. The films were soaked in the 3% v/v IPA/DCM mixture for 30 min and repeated a second time in fresh 3% v/v IPA/DCM. The resulting transmissive-blue films were shown to be in the conductive (i.e., oxidized) state by four-point probe measurements. It was discovered that the 3% v/v IPA/DCM rinse solution was ideal for creating smooth and crack free films. Initial attempts at rinsing films with 100% IPA, or other alcohols, gave extensively cracked films. The nature of the cracking suggested that IPA was rapidly swelling the films and/or extracting PMA too quickly, resulting in unmanageable stresses in the films. We hypothesized that the cracking could be prevented by slowing the rate of swelling and/or the PMA extraction rate. Decreasing the concentration of IPA to ∼3% v/v in DCM, a solvent that PMA is insoluble in, we found the cracking to consistently disappear. For purposes of comparison, PEDOT films were electrochemically grown on ITO coated glass slides from an acetonitrile solution containing 0.02 M EDOT and 0.1 M $LiClO_4$. This was done by setting $V = 1.125$ (vs Ag/Ag^+) and passing 0.0386 C of charge to an immersed electrode having an area of ca. 1 cm^2. This gave nominally 200 nm thick films.

Characterization. *UV−Vis Spectroscopy*. The chemical polymerization of EDOT with PMA was investigated in bulk acetonitrile and THF solution using a 1.0 cm quartz cuvette containing a 0.9 cm quartz insert. The ca. 0.1 cm path length allowed higher concentrations to be studied. Spectra were acquired at room temperature on an Agilent 8453 UV−vis spectrometer.

Cyclic Voltammetric measurements were performed with a CH Instruments CHI-760 workstation potentiostat that was controlled by a PC. Unless otherwise noted, a three-electrode setup was used, using a platinum rod auxiliary electrode and fluorine-doped tin-oxide (FTO) working electrode. Ag/AgCl and Ag/Ag^+(MeCN) reference electrodes were used in aqueous and nonaqueous solution, respectively. These measurements were performed in aqueous acid (0.5 M H_2SO_4) and nonaqueous solution (acetonitrile) with 0.1 M $(TBA)PF_6$ as supporting electrolyte.

Four-point probe measurements were performed using a Signatone four-point probe apparatus attached to a Fluke 87 True rms multimeter and constant-current source system (CHI-760 workstation controlled by a PC). The spring loaded tungsten carbide probe contacts were spaced 0.040 in. apart. The electrical conductivity σ (Ω^{-1} cm^{-1}) was expressed by $\sigma = ln2i/\pi dV$ where d is the thickness of the films determined with an Alpha Step 500 general source profiler, i is the current passed through the outer probes, and V is the voltage across the inner probes. Current was applied within the range of 1.0×10^{-8}-8.0×10^{-7} A and voltages were obtained within the range of 0 to 9 V.

Scanning electron microscopy (SEM) images were collected using a Cambridge Instruments Stereoscan 120 SEM, equipped with a secondary electron (SE) detector, a four-quadrant semiconductor backscatter electron (SBE) detector, and an EDAX Genesis 4000 energy dispersive X-ray spectrometer (EDS) at an accelerating voltage of 20 keV. No Au/carbon was necessary unless otherwise specified.

X-ray photoelectron spectroscopy (XPS) data was acquired on a Kratos Axis Ultra XPS system using a monochromated Al Kα source at 225 W.

Results and Discussion

Solution Kinetics. The UV−vis spectrum of fully reduced/neutral PEDOT exhibits a bandgap of 1.6−1.7 eV with a λ_{max} of ∼610 nm, while oxidized/p-doped PEDOT exhibits a polaronic band at λ_{max} of ~800 nm.[4] The rate of formation of p-doped PEDOT was monitored by following the temporal evolution of this polaronic band in acetonitrile, THF, and a 50/50 mixture of acetonitrile/THF containing 0.2 M EDOT and 0.5 M PMA as shown in Figure 1. The temporal rise in absorbance at ~800 nm is attributed to increasing levels of p-doped PEDOT in the polymerization mixture. Solutions containing 0.2 M EDOT and varying concentrations of PMA (0.05−0.45 M) were also studied, and exhibited similar behavior to that shown in Figure 1. A small rate dependence on PMA concentration was noted (see Figure SI-1, Supporting Information). To study the effect of solvent on reaction rate, solutions containing 0.2 M EDOT and 0.5 M PMA were studied in a quartz cell with a path length of 0.1 cm. As shown in Figure 1, the rate of formation of p-doped PEDOT is greatest in acetonitrile, followed by a 50/50 mixture of acetonitrile/THF and finally THF. The rate of formation of p-doped PEDOT in acetonitrile was sufficiently fast that a dark green/black precipitate was observed within ~5 min of mixing, while the rate was sufficiently slow in THF that a homogeneous solution was maintained for at least 30 min. The visual observation of precipitation in acetonitrile coincides with the bend in the acetonitrile trace of Figure 1, suggesting that the precipitation of p-doped PEDOT from acetonitrile drastically reduces the soluble concentration of species involved in polymerization, and therefore the rate. These results demonstrate the influence of solvent on solution metastability, indicating that the time available for processing solutions of EDOT monomer and PMA oxidant, after they are mixed, is strongly dependent upon the solvent. For example, films prepared via *in situ* polymerization of EDOT in acetonitrile must be spun within ca. 5 min after mixing EDOT and PMA to avoid polymer precipitation, whereas films prepared from THF solutions are stable for at least 30 min.

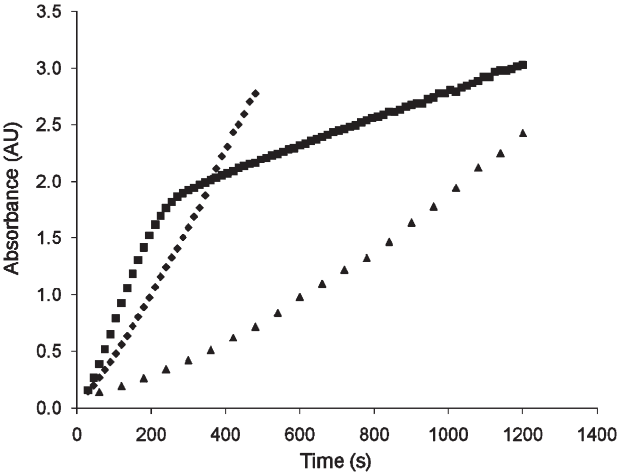

Figure 1. Temporal evolution of PEDOT−PMA solution spectra at 800 nm during the polymerization of 0.2 M EDOT and 0.5 M phosphomolybdic acid in acetonitrile (■), THF (▲) and a 50:50 mixture of acetonitrile:THF (◆).

Film Morphology. PEDOT−PMA thin films were prepared by spin-coating mixtures containing 0.2 M EDOT and 0.05−0.50 M PMA in acetonitrile and rinsed with an ~3% v/v IPA/DCM solution before examining their morphology with scanning electron microscopy (SEM). Generally, films of increasing thickness were formed with increasing amounts of PMA added to the mixture. This is attributed to either increasing solution viscosity and/or increasing polymer/PMA deposition with increasing amounts of PMA added to the mixture. SEM images of PEDOT−PMA films prepared from acetonitrile solutions containing 0.2 M EDOT and 0.05−0.30 M PMA onto nonconducting glass substrates are smooth, uniform, homogeneous, crack and pinhole free on the micrometer scale as illustrated in Figure 2A, while SEM images of PEDOT−PMA films prepared from acetonitrile solutions containing 0.2 M EDOT and 0.35−0.50 M PMA exhibited a heterogeneous morphology as illustrated in Figure 2B. Similar results were observed with films prepared from THF. It was observed that smooth, uniform, homogeneous, crack and pinhole free films could be consistently prepared on nonconducting glass substrates by rinsing them with 3% v/v IPA/DCM. If a more polar solvent or solvent mixture (i.e., 100% alcohol or greater than 5% v/v IPA/DCM) was used, then smooth, uniform, homogeneous, crack and pinhole free films could not be consistently generated. XPS analysis of the washed films gave a Mo 3d to S 2p atomic ratio of ~3:1 (see Figure SI-2, Supporting Information). This is consistent with one $H_2PMo_{12}O_{40}$ anion charge balancing one positive charge delocalized over four EDOT units. This suggests that the excess PMA was removed from the films during the washing step. In principle, other oxidants such as $FeCl_3$ may be used, however, oxidants with oxidation potentials close to the oxidation potential of the monomer are necessary in order to maintain solution metastability, and hence the processability and production of smooth defect free films.[25]

Film Conductivity. Conductivity measurements were performed with a four-point probe device and were found to vary over an order of magnitude (0.02−0.47 S/cm), depending on the concentration of PMA in the mixture. The conductivities are similar to those reported for powders of PEDOT−PSS compressed into pellets.[26] Generally, films with the largest conductivity were prepared using equimolar quantities of EDOT and PMA, indicating that control over

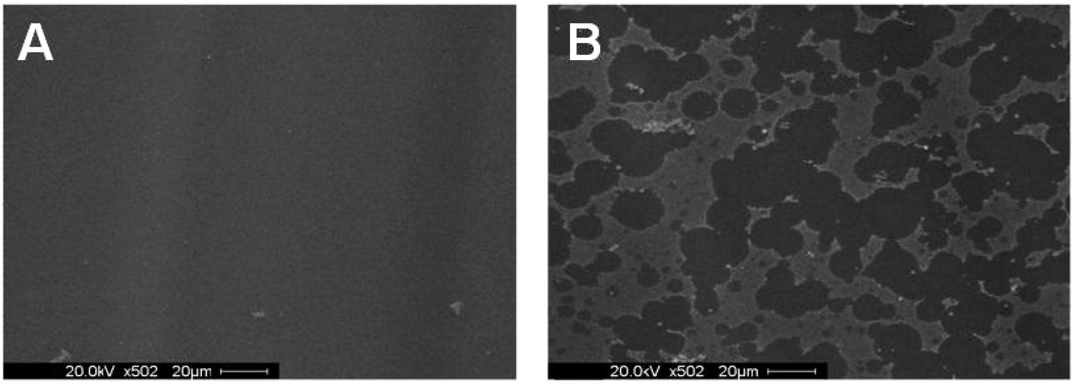

Figure 2. SEM images of PEDOT−PMA spin-coated films prepared from acetonitrile solutions containing 0.2 M EDOT and (A) 0.05 M PMA and (B) 0.35 M PMA.

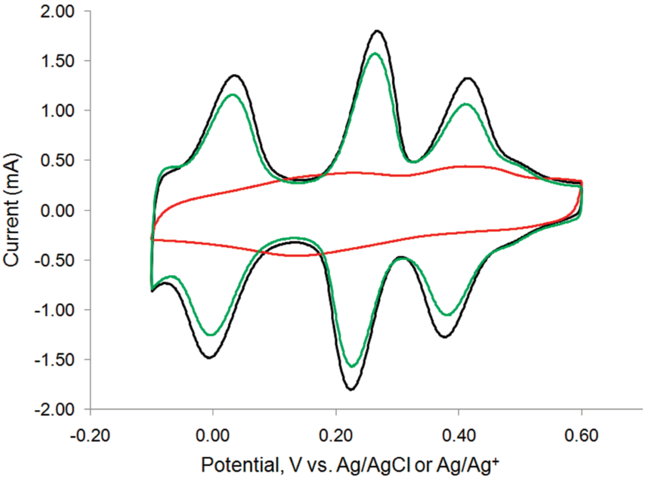

Figure 3. Cyclic voltammograms of PEDOT−PMA films deposited onto FTO electrodes by spin-coating acetonitrile solutions containing 0.2 M EDOT and 0.15 M PMA. The pristine PEDOT−PMA film was first cycled in 0.5 M H_2SO_4 (black), followed by cycling in 0.1 M (TBA)PF_6 acetonitrile (red), and returned to and cycled in 0.5 M H_2SO_4 (green). A total of five scans at a scan rate of 50 mV/s was applied to each solution. Potentials measured in 0.5 M H_2SO_4 were referenced to Ag/AgCl and potentials in 0.1 M (TBA)PF_6 acetonitrile were referenced to Ag/Ag^+.

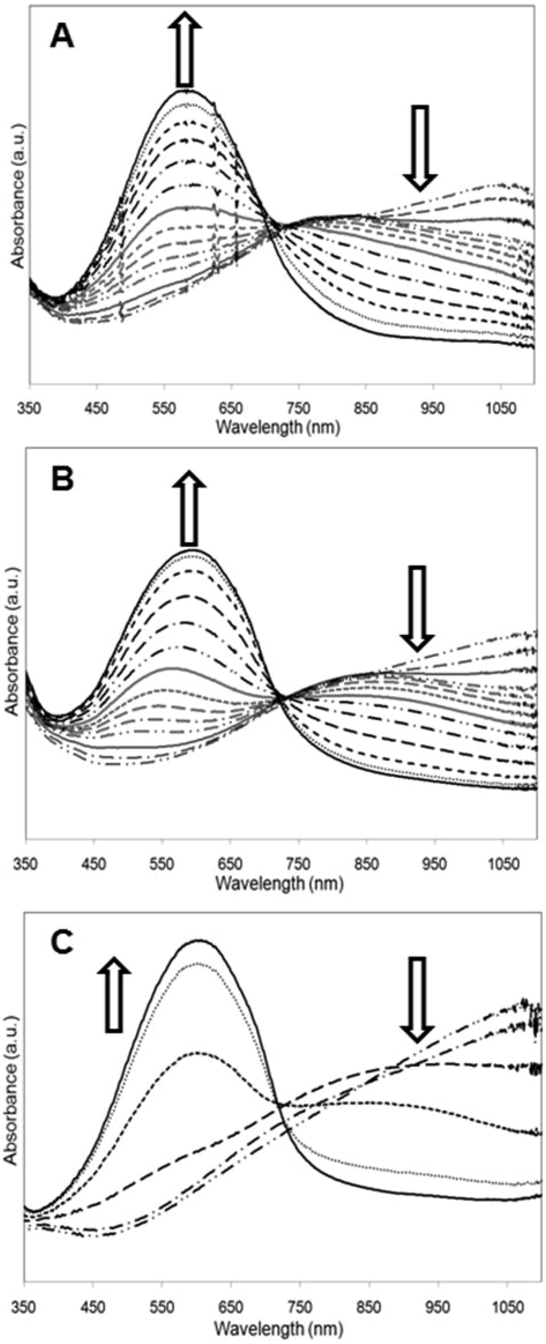

Figure 4. Spectroelectrochemistry of PEDOT−PMA films were conducted on FTO coated glass substrates. The films were prepared by spin-coating acetonitrile or THF solutions containing 0.2 M EDOT and 0.15 M PMA. Spectroelectrochemistry of electrochemically grown PEDOT-ClO_4 films were conducted on ITO coated glass substrates. All spectroelectrochemistry measurements were conducted in 0.1 M (TBA)PF_6/acetonitrile solution. (A) PEDOT−PMA film chemically grown from acetonitrile and potentials scanned from -1.0 to 0.6 V vs Ag/Ag^+ and (B) PEDOT−PMA film chemically grown from THF and potentials scanned from -1.0 to 0.6 V vs Ag/Ag^+ (C) and electrochemically grown PEDOT-ClO_4 on ITO and potentials scanned from -1.4 to 0.6 V vs Ag/Ag^+.

the molar ratio of EDOT/PMA is critical to achieving optimal conductivities (see Figure SI-3, Supporting Information). Lower conductivity films prepared from solutions containing a significantly higher ratio of EDOT/PMA is consistent with incomplete polymerization and/or production of significant amounts of PEDOT polymer in its reduced nonconductive state, while lower conductivity films prepared from solutions containing significantly lower ratios of EDOT/PMA is consistent with significant amounts of nonconductive PMA remaining trapped within the film, or with a more diffuse porous film structure generated due to a templating effect of excess PMA. The optimal conductivity observed when equimolar quantities of EDOT and PMA were used likely balances these issues.

Electrochemistry. A cyclic voltammogram (CV) of a PEDOT−PMA film that was prepared by spin-coating acetonitrile solutions containing 0.2 M EDOT and 0.15 M PMA onto conductive fluorine doped tin oxide (FTO) coated glass slides is shown in Figure 3. The potential was cycled from -0.1 to -0.6 V vs Ag/AgCl. In aqueous acid solution facile redox current attributed to three $2e^-/2H^+$ oxidation and three $2e^-/2H^+$ reduction peaks of PMA dominate the electrochemistry,[27] indicating that PMA is incorporated into the film in such a manner that good electronic communication is established between the electronically conducting PEDOT and the electronically insulating PMA. The redox peaks of PEDOT are not visible due to the dominance of PMA peaks, similar to previous reports.[25,28] Repeated CV cycling of the film (500 cycles) in aqueous acid solution results in an ~20% drop in anodic peak current (see Figure SI-4, Supporting Information), suggesting that PMA is slowly leaching from the film. This is supported by UV−vis spectroscopy of the solution which shows the presence of PMA (see Figure SI-5, Supporting Information). Cycling a PEDOT−PMA film in 0.1 M (TBA)PF_6 acetonitrile solution shows that PMA is no longer redox active under these conditions (Figure 3). The redox peaks are attributed to facile conversion of neutral PEDOT to polaronic PEDOT at intermediate potentials, followed by conversion of polaronic PEDOT to bipolaronic PEDOT at higher potentials.[29,30] However, when the film is returned to aqueous acid solution, and cycled, the PMA peaks are again redox active.[25,31] Attempts to completely remove PMA from the film (e.g., repeated cycling) were unsuccessful, presumably due to its steric bulk. However, PMA is a well-known catalyst, so its presence in PEDOT is expected to be beneficial in applications requiring its catalytic properties. Only in cases where its redox behavior may complicate performance would it be necessary to remove PMA.

UV−Vis Spectroelectrochemistry. Using the above CV experiments as a means of determining the correct potential ranges for switching and evaluating the stability of the electroactivity of the PEDOT−PMA film, *in situ* spectroelectrochemical experiments were conducted as shown in Figure 4. PEDOT was deposited either chemically in the form of PEDOT−PMA or electrochemically in the form of PEDOT-ClO_4 onto conducting glass substrates, rinsed in 3% v/v IPA/DCM solution, and allowed to dry at room temperature. Electrochemically grown PEDOT-ClO_4 films were grown onto conducting ITO coated glass substrates for comparison purposes. Chemically grown films were deposited onto conducting FTO glass substrates from acetonitrile or THF solutions containing 0.2 M EDOT and 0.15 M PMA. Films were placed into a 0.1 M $(TBA)PF_6$ acetonitrile solution referenced to Ag/Ag^+ and electrochemically oxidized or reduced stepwise by increasing or decreasing the potential. The spectroelectrochemistry of PEDOT−PMA films grown chemically from acetonitrile and THF are shown in Figure 4A-B, while an electrochemically grown PEDOT-ClO_4 film is shown in Figure 4C. Formation of polarons is attributed to the increase in absorption at ~900 nm in conjunction with the decrease in intensity of the $\pi-\pi^*$ bands at ~600 nm through a well-defined isosbestic point. The $\pi-\pi^*$ electronic transition of PEDOT−PMA films grown chemically from THF or acetonitrile are similar to each other ($\lambda_{max} \sim 590$ nm), while an electrochemically grown PEDOT-ClO_4 is ca. 10 nm bathochromically shifted from the chemically grown films ($\lambda_{max} \sim 600$ nm). This bathochromic shift may be attributed to either lower degrees of polymerization in the chemically grown films or steric interactions originating from the bulky PMA counterions in the PEDOT−PMA films, which inhibit intramolecular $\pi-\pi$ interactions. Presumably this is absent in the PEDOT-ClO_4 films containing the much smaller perchlorate counterion, therefore allowing for increased intramolecular $\pi-\pi$ interactions and resulting increased planarity. The nature of the polymerization solvent has little influence on the resulting spectroelectrochemistry of the films. This is consistent with the similar morphology observed for films prepared from THF or acetonitrile. The color of PEDOT−PMA films ranged from deep-blue/purple in their reduced states to transmissive gray/blue in their oxidized state. This suggests that PEDOT−PMA films are good candidates for electrochromic devices and applications requiring transmissive electrodes. The spectroelectrochemistry data demonstrates that good quality, switchable PEDOT−PMA films can be prepared through *in situ* chemical polymerization.

Conclusions

We have been able to synthesize, in one-step, conductive (0.02−0.47 S/cm), uniform, smooth, homogeneous, transmissive, crack and pinhole free PEDOT−PMA films possessing well-defined spectroelectrochemistry through *in situ* metastable polymerization, by spin-coating organic-solvent processable mixtures of EDOT and PMA onto either nonconductive or conductive glass substrates. This straightforward organic-solvent processable method of preparing high quality PEDOT films should be applicable to current and future technologies requiring organic-solvent compatible processes and is currently being explored in our laboratory. We have been able to demonstrate that the redox current associated with PMA is retained in the films when they are electrochemically cycled in either aqueous acid or organic electrolyte. We are currently exploring methods to remove or swap PMA from PEDOT−PMA with other inorganic ions as a way to modify the conductivity, porosity, and chemical properties of these films in order to fine-tune chemical selection for olfactory sensor arrays.

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Supporting Information Available: Figures showing plots of the data illustrating the influence of PMA on reaction rate and film conductivity as well as XPS characterization of the films and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1977**, 578.
(2) Heeger, A. J. *Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials.* http://nobelprize.org/nobel_prizes/chemistry/laureates2000/heeger-lecture.pdf.
(3) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(4) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.
(5) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
(6) Carter, S. A.; Angelopoulos, M.; Karg, S.; Brock, P. J.; Scott, J. C. *Appl. Phys. Lett.* **1997**, *70*, 2067.
(7) Krebs, F. C. *Sol. Energ. Mat. Sol. C.* **2008**, *92*, 715.
(8) Jonas, F.; Morrison, J. T. *Synth. Met.* **1997**, *85*, 1397.
(9) Andersson, P.; Forchheimer, R.; Tehrani, P.; Berggren, M. *Adv. Funct. Mater.* **2007**, *17*, 3074.
(10) Chen, L.; Yuan, C. Z.; Dou, H.; Gao, B.; Chen, S. Y.; Zhang, X. G. *Electrochim. Acta* **2009**, *54*, 2335.
(11) Michalska, A.; Maksymiuk, K. *Anal. Chim. Acta* **2004**, *523*, 97.
(12) Setti, L.; Fraleoni-Morgera, A.; Ballarin, B.; Filippini, A.; Frascaro, D.; Piana, C. *Biosens. Bioelectron.* **2005**, *20*, 2019.
(13) Lefebvre, M. C.; Qi, Z. G.; Pickup, P. G. *J. Electrochem. Soc.* **1999**, *146*, 2054.
(14) Freund, M. S.; Lewis, N. S. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 2652.
(15) Kim, T.; Suh, M.; Kwon, S. J.; Lee, T. H.; Kim, J. E.; Lee, Y. J.; Kim, J. H.; Hong, M.; Suh, K. S. *Macromol. Rapid Commun.* **2009**, *30*, 1477.
(16) Groenendaal, L.; Zotti, G.; Jonas, F. *Synth. Met.* **2001**, *118*, 105.
(17) Pettersson, L. A. A.; Carlsson, F.; Inganas, O.; Arwin, H. *Thin Solid Films* **1998**, *313*, 356.
(18) Winther-Jensen, B.; West, K. *Macromolecules* **2004**, *37*, 4538.
(19) Winther-Jensen, B.; Chen, J.; West, K.; Wallace, G. *Macromolecules* **2004**, *37*, 5930.
(20) Lock, J. P.; Im, S. G.; Gleason, K. K. *Macromolecules* **2006**, *39*, 5326.
(21) Chen, J. H.; Dai, C. A.; Chiu, W. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1662.
(22) Fabretto, M.; Zuber, K.; Hall, C.; Murphy, P. *Macromol. Rapid Commun.* **2008**, *29*, 1403.
(23) Fabretto, M.; Muller, M.; Zuber, K.; Murphy, P. *Macromol. Rapid Commun.* **2009**, *30*, 1846.
(24) Freund, M. S.; Karp, C.; Lewis, N. S. *Inorg. Chim. Acta* **1995**, *240*, 447.
(25) Bravo-Grimaldo, E.; Hachey, S.; Cameron, C. G.; Freund, M. S. *Macromolecules* **2007**, *40*, 7166.
(26) Lefebvre, M.; Qi, Z. G.; Rana, D.; Pickup, P. G. *Chem. Mater.* **1999**, *11*, 262.
(27) Sadakane, M.; Steckhan, E. *Chem. Rev.* **1998**, *98*, 219.
(28) White, A. M.; Slade, R. C. T. *Electrochim. Acta* **2004**, *49*, 861.
(29) Chen, X. W.; Inganas, O. *J. Phys. Chem.* **1996**, *100*, 15202.
(30) Snook, G. A.; Peng, C.; Fray, D. J.; Chen, G. Z. *Electrochem. Commun.* **2007**, *9*, 83.
(31) Suppes, G. M.; Deore, B. A.; Freund, M. S. *Langmuir* **2008**, *24*, 1064.